

CLAIMS

- 1) Emulgator-free microgel dispersion, obtainable by intermolecular or intramolecular crosslinking in an aqueous medium of a pre-polymer, wherein the pre-polymer has

- at least two capped NCO groups;
- at least three groups having at least one active hydrogen atom bonded to a nitrogen atom;
- at least one segment in the backbone of the polyester originating from a triol, polyol, linear and/or branched polyester polyol; and
- at least one group capable of forming anions

and wherein in the intermolecular or intramolecular crosslinking the nitrogen atoms carrying at least one active hydrogen atom react with the blocked NCO groups while forming urea compounds and releasing the blocking agent.

- 2) Emulgator-free microgel dispersion, obtainable by intermolecular or intramolecular crosslinking in an aqueous medium of a pre-polymer, wherein the pre-polymer has

- at least three capped NCO groups;
- at least two groups having at least one active hydrogen atom bonded to a nitrogen atom;
- at least one segment in the backbone of the polyester originating from a triol, polyol, linear and/or branched polyester polyol; and
- at least one group capable of forming anions

and wherein in the intermolecular or intramolecular crosslinking the nitrogen atoms carrying at least one active hydrogen atom react with the blocked NCO groups while forming urea compounds and releasing the blocking agent.

- 3) Microgel dispersion according to claim 1 or 2, wherein more than 70% of the groups with at least one active hydrogen atom bonded to a nitrogen atom are reacted while forming polyurea compounds.

- 4) Microgel dispersion according to one of the preceding claims, wherein the group having at least one hydrogen atom bonded to a nitrogen atom is an NH_2 group.
- 5) Microgel dispersion according to one of the preceding claims, wherein the pre-polymer has
 - a number-average molecular weight of more than 2,000;
 - an acid number between 10 and 30 mg KOH/g;
 - at least one segment originating from a diisocyanate as the hard segment.
- 6) Microgel dispersion according to one of the preceding claims, wherein the triol has 3 to 24 carbon atoms and is preferably trimethylolpropane.
- 7) Microgel dispersion according to one of the preceding claims, wherein the polyol has 3 to 12 carbon atoms and is preferably di-trimethylolpropane.
- 8) Microgel dispersion according to one of the preceding claims, wherein the linear and/or branched polyester polyol can be obtained from the polycondensation of a polycarboxylic acid having at least one diol or polyol.
- 9) Microgel dispersion according to claim 8, wherein the linear or branched polyester polyol has a number-average molecular weight between 300 and 4,000 and a hydroxyl number between 28 and 580.
- 10) Microgel dispersion according to one of the preceding claims, wherein the capped NCO groups are the same or different and result from the reaction of a diisocyanate such as 1,1-methylenebis(4-isocyanatocyclohexane) (4,4'-dicyclohexylmethane diisocyanate, Desmodur W), hexamethylene diisocyanate (HMDI, 1,6-diisocyanate hexane, Desmodur H), isophoron-diisocyanate IPDI, 3,5,5-tri-methyl-1-isocyanato-3-isocyanatomethylcyclohexane), 1,4-cyclohexyldiisocyanate (CHDI, trans,-trans-1,4-diisocyanato-

cyclohexane), in particular 1,3-bis(1-isocyanato-1-methylethyl)benzene (TMXDI, m-tetramethylxylylenediisocyanate), with a capping agent, in particular with methylethylketoxime.

- 11) Microgel dispersion according to one of the preceding claims, wherein the group capable of forming anions originates from dimethylpropionic acid, 9,10-dihydroxystearic acid and/or from a polyester polyol having at least one group capable of forming anions.
- 12) Microgel dispersion according to one of the preceding claims, wherein the number-average molecular weight of the pre-polymer is at the most 10,000, preferably between 3,000 and 7,000.
- 13) Microgel dispersion according to one of the preceding claims, wherein the crosslinking is carried out in the presence of an additional polymer with an OH number between 30 and 400 and an acid number between 1 and 150, selected from the group of polyacrylates, polyesters and polyurethanes.
- 14) Microgel dispersion according to one of the preceding claims, wherein the crosslinking together with an emulsion polymerization, using
 - at least one monomer compound which contains at least one radically polymerizable double bond, and
 - at least one monomer compound containing hydroxyl groups which contains at least one radically polymerizable double bond.
- 15) Microgel dispersion according to one of the preceding claims, wherein the reaction mixture originating from the crosslinking subsequently undergoes emulsion polymerization of at least one monomer compound which contains at least one radically polymerizable double bond and in particular has at least one hydroxyl group.
- 16) Microgel dispersion according to claim 14 or 15, wherein emulsion polymerization is carried out in the presence of additionally at least one

monomer compound without hydroxyl groups which contains at least one radically polymerizable double bond.

- 17) Emulgator-free microgel dispersion, obtainable by crosslinking of a polymer A dispersed in an aqueous medium and a polymer B, wherein

- polymer A has at least two capped NCO groups;
- polymer B has at least three groups having at least one active hydrogen atom bonded to a nitrogen atom
- and wherein polymer A and/or polymer B has
- at least one segment in the backbone of the polyester originating from a diol, polyol, polyether and/or a polyester polyol; and
- at least one group capable of forming anions

and wherein during crosslinking the nitrogen atoms carrying at least one active hydrogen atom react with the blocked NCO groups while forming urea compounds and releasing the blocking agent.

- 18) Emulgator-free microgel dispersion, obtainable by crosslinking of a polymer A dispersed in an aqueous medium with a polymer B, wherein

- polymer A has at least three capped NCO groups;
- polymer B has at least two groups having at least one active hydrogen atom bonded to a nitrogen atom
- and wherein polymer A and/or polymer B has
- at least one segment in the backbone originating from a diol, polyol, polyether and/or a polyester polyol; and
- at least one group capable of forming anions

and wherein during crosslinking the nitrogen atoms carrying at least one active hydrogen atom react with the blocked NCO groups while forming urea compounds and releasing the blocking agent.

- 19) Emulgator-free microgel dispersion, obtainable by crosslinking of a polymer A dispersed in an aqueous medium with a polyamine, wherein

- polymer A has at least two capped NCO groups;

- the polyamine has at least three groups having at least one active hydrogen atom bonded to a nitrogen atom
- and wherein the polymer has
- at least one segment in the backbone of the polyester originating from a diol, polyol, polyether and/or a polyester polyol; and
- at least one group capable of forming anions

and wherein during crosslinking the nitrogen atoms carrying at least one active hydrogen atom react with the blocked NCO groups while forming urea compounds and releasing the blocking agent.

20) Emulgator-free microgel dispersion, obtainable by crosslinking of a polymer A dispersed in an aqueous medium with a polyamine, wherein

- polymer A has at least three capped NCO groups;
- the polyamine has at least two groups having at least one active hydrogen atom bonded to a nitrogen atom

and wherein the polymer has

- at least one segment in the backbone of the polyester originating from a diol, polyol, polyether and/or a polyester polyol; and
- at least one group capable of forming anions

and wherein during crosslinking the nitrogen atoms carrying at least one active hydrogen atom react with the blocked NCO groups while forming urea compounds and releasing the blocking agent.

21) Microgel dispersion according to one of the claims 17 to 20, wherein the number-average molecular weight of polymer A and/or polymer B is at most 10,000, preferably between 2,000 and 8,000.

22) Microgel dispersion according to one of the claims 17 to 21, wherein polymer A additionally contains two non-capped NCO groups and polymer A undergoes chain elongation/extension before crosslinking with polymer B or a polyamine, with a diamine and/or polyamine.

- 23) Microgel dispersion according to claim 22, wherein the diamine or polyamine has at least one group capable of forming anions.
- 24) Microgel dispersion according to claim 23, wherein the group capable of forming anions originates exclusively from the diamine or polyamine.
- 25) Microgel dispersion according to claim 24, wherein the group capable of forming anions is a sulphonic acid group.
- 26) Emulgator-free microgel dispersion according to claim 25, wherein at least one group capable of forming anions is present per 8,000 number-average mole weight units.
- 27) Emulgator-free microgel dispersions, obtainable by crosslinking of a polymer B dispersed in an aqueous medium with a capped polyisocyanate, wherein
 - the capped isocyanate is not dispersible in water and has at least two capped NCO groups;
 - polymer B has at least three groups having at least one active hydrogen atom bonded to a nitrogen atom
 - and wherein polymer B has
 - at least one segment in the backbone of the polyester originating from a diol, polyol, polyether and/or a polyester polyol; and
 - at least one group capable of forming anions
 and wherein during crosslinking the nitrogen atoms carrying at least one active hydrogen atom react with the blocked NCO groups while forming urea compounds and releasing the blocking agent.
- 28) Emulgator-free microgel dispersions, obtainable by crosslinking a polymer B dispersed in an aqueous medium with a polyamine, wherein
 - the capped isocyanate is not dispersible in water and has at least two capped NCO groups;

- polymer B has at least two groups having at least one active hydrogen atom bonded to a nitrogen atom
- and wherein polymer B has
- at least one segment in the backbone of the polyester originating from a diol, polyol, polyether and/or a polyester polyol; and
- at least one group capable of forming anions

and wherein during crosslinking the nitrogen atoms carrying at least one active hydrogen atom react with the blocked NCO groups while forming urea compounds and releasing the blocking agent.

- 29) Microgel dispersion according to one of the claims 17 to 28, wherein an additional polymer C with an OH number between 30 and 400 and an acid number between 1 and 150 is crosslinked, selected from the group of polyacrylates, polyesters and polyurethanes.
- 30) Microgel dispersion according to one of the claims 17 to 29, wherein the crosslinking is carried out together with an emulsion polymerization of at least one monomer compound containing hydroxyl groups which contains at least one radically polymerizable double bond.
- 31) Microgel dispersion according to one of the claims 17 to 30, wherein the reaction mixture originating from the crosslinking subsequently undergoes emulsion polymerization of at least one monomer compound which contains at least one radically polymerizable double bond and in particular at least one hydroxyl group.
- 32) Microgel dispersion according to claim 30 or 31, wherein the emulsion polymerization is carried out in the presence additionally of at least one monomer compound without hydroxyl groups which contains at least one radically polymerizable double bond.

- 33) Microgel dispersion according to one of the claims 17 to 32, wherein polymer A and/or B has
- a number-average molecular weight of more than 800;
 - an acid number between 10 and 70 mg KOH/g.
- 34) Microgel dispersion according to one of the claims 17 to 33, wherein the diol or polyol has 2 to 36 carbon atoms and is preferably selected from the group of trimethylolpropanemonoallyether, di-trimethylolpropane and hydroxylated fatty acid compounds.
- 35) Microgel dispersion according to one of the claims 17 to 34, wherein the polyester polyol has a number-average molecular weight between 200 and 6,000, an OH number between 20 and 550 and an acid number less than 5.
- 36) Microgel dispersion according to one of the claims 17 to 35, wherein the group capable of forming anions originates from dimethylolpropionic acid and/or 9,10-dihydroxystearic acid.
- 37) Microgel dispersion according to one of the claims 17 to 35, wherein the group capable of forming anions originates from a polyester polyol which has at least one free carboxyl group on average per molecule which originates from trimellithic acid, trimellithic acid anhydride, dimethylolpropionic acid or dihydroxystearic acid.
- 38) Microgel dispersion according to one of the claims 17 to 37, wherein at least one of the groups of the polymer with at least one active hydrogen atom bonded to a nitrogen atom originates from a di- or polyamine, in particular from 2-methyldiaminopentane, ethylenediamine, N,N-diethylenetriamine, adipic acid bishydrazide or hydrazine segment.
- 39) Microgel dispersion according to one of the claims 17 to 38, wherein the capped NCO groups are different or the same and originate from the reaction of a diisocyanate such as TMXDI (m-

tetramethylxylylenediisocyanate), 1,1-methylenebis(4-isocyanatocyclohexane), (4,4'-dicyclohexylmethanediisocyanate, Desdomur W), hexamethylenediisocyanate (HMDI, 1,6-diisocyanatohexane, Desmodur H), isophorondiisocyanate (IPDI, 3,5,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane), 1,4-cyclohexyldiisocyanate (CHDI, trans-, trans-1,4-diisocyanatocyclohexane) and/or form aliphatic triisocyanates such as N-isocyanatohexylaminocarbonyl-N,N'-bis(isocyanatohexyl)urea (Desmodur N), 2,4,6-trioxo-1,3,5-tris(6-isocyanatohexyl)hexahydro-1,3,5-triazine (Desmodur N3300), 2,4,6-trioxo-1,3,5-(5-isocyanato-1,3,3-trimethylcyclohexylmethyl)hexahydro-1,3,5-triazine (Desmodur Z4370) with a capping agent, in particular with methylethylketoxime.

- 40) Emulgator-free and acrylate-modified microgel dispersion, obtainable by emulsion polymerization of at least one monomer compound (A) containing hydroxyl groups which contains at least one radically polymerizable double bond in the presence of an aqueous dispersion of a polymer (B), the latter containing

- at least two capped NCO groups;
- at least one segment in the backbone of the pre-polymer originating from a diol, polyol, polyether and/or polyester polyol; and
- at least one group capable of forming anions,

wherein during emulsion polymerization the hydroxyl groups of the monomer compound (A) react with the capped NCO groups of polymer (B) while forming urea compounds and releasing the blocking agent.

- 41) Microgel dispersion according to claim 40, wherein the emulsion polymerization is carried out additionally in the presence of at least one monomer compound (C) free of hydroxyl groups which contains at least one radically polymerizable double bond.

- 42) Microgel dispersion according to claim 40 or 41, wherein the emulsion polymerization is carried out in the presence of an additional polymer (D) with an OH number between 30 and 400 and an acid number between 1

and 150, selected from the group of polyacrylates, polyesters and polyurethanes.

- 43) Microgel dispersion according to one of the claims 40 to 42, wherein the reaction mixture originating from the emulsion polymerization undergoes further emulsion polymerization with at least one monomer compound which contains at least one radically polymerizable double bond and in particular has at least one hydroxyl group.
- 44) Microgel dispersion according to one of the claims 40 to 43, wherein the additional emulsion polymerization is carried out in the presence of at least one monomer compound without hydroxyl groups, which contains at least one radically polymerizable double bond.
- 45) Microgel dispersion according to one of the claims 40 to 44, wherein polymer (B) has
 - a number-average molecular weight of more than 800;
 - an acid number between 20 and 150 mg KOH/g.
- 46) Microgel dispersion according to one of the claims 40 to 45, wherein the diol or polyol has 2 to 36 carbon atoms and is preferably selected from the group of trimethylolpropane monoallylether, di-trimethylolpropane and hydroxylated fatty acid compounds.
- 47) Microgel dispersion according to one of the claims 40 to 46, wherein the polyester polyol has a number-average molecular weight between 200 and 6,000, an OH number between 20 and 550 and an acid number less than 5.
- 48) Microgel dispersion according to one of the claims 40 to 47, wherein the group capable of forming anions originates from dimethylolpropionic acid and/or 9,10-dihydroxyl stearic acid.

- 49) Microgel dispersion according to one of the claims 40 to 48, wherein the group capable of forming anions originates from a polyester polyol which has at least one free carboxyl group on average per molecule which originates from trimellithic acid, trimellithic acid anhydride, dimethylolpropionic acid or dihydroxystearic acid.
- 50) Microgel dispersion according to one of the claims 40 to 49, wherein the capped NCO groups are the same or different and originate from the reaction of a diisocyanate such as TMXDI (m-tetramethylxylylenediisocyanate), 1,1-methylenebis(4-isocyanatocyclohexane), 4,4'-dicyclomethanediisocyanate, Desmodur W), hexamethylenediisocyanate (HMDI, 1,6-diisocyanatohexane, Desmodur H), isophorondiisocyanate (IPDI, 3,5,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane), 1,4-cyclohexyldiisocyanate (CHDI, trans,-trans-1,4-diisocyanatocyclohexane) and/or from aliphatic triisocyanates such as N-isocyanatohexylaminocarbonyl-N,N-bis-(isocyanatohexyl)urea (Desmodur N), 2,4,6-trioxo-1,3,5-tris(6-isocyanatohexyl)-hexahydro-1,3,5-triazine (Desmodur N3300), 2,4,6-trioxo-1,3,5-tris(5-isocyanato-1,3,3-trimethylcyclohexymethyl)hexahydro-1,3,5-triazine (Desmodur Z4370) with a capping agent, in particular with methylethylketoxime.
- 51) Microgel dispersion according to one of the claims 40 to 50, wherein the number-average molecular weight of polymer (B) is at the most 10,000, preferably between 1,000 and 8,000.
- 52) Microgel dispersion according to one of the preceding claims, wherein the microgel has an acid number between 10 and 50 mg KOH/g, in particular between 10 and 30 mg KOH/g.
- 53) Use of a microgel dispersion according to one the preceding claims to produce a multilayer coating, in particular in the automobile industry.
- 54) Use according to claim 53 for producing a basecoat.

- 55) Use according to claim 53 or 54, wherein the amount of microgel, relative to the solids of the coat obtainable from it, is between 20 and 85%, preferably between 20 and 65%.